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Correlated $\delta^{18}O$ and [Ti] in lunar zircons: a terrestrial perspective for magma temperatures and water content on the Moon

John W. Valley · Michael J. Spicuzza · Takayuki Ushikubo

Abstract Zircon grains were separated from lunar regolith and rocks returned from four Apollo landing sites, and analyzed in situ by secondary ion mass spectrometry. Many regolith zircons preserve magmatic $\delta^{18}O$ and trace element compositions and, although out of petrologic context, represent a relatively unexplored resource for study of the Moon and possibly other bodies in the solar system. The combination of oxygen isotope ratios and [Ti] provides a unique geochemical signature that identifies zircons from the Moon. The oxygen isotope ratios of lunar zircons are remarkably constant and unexpectedly higher in $\delta^{18}O$ (5.61 ± 0.07 ‰ VSMOW) than zircons from Earth's oceanic crust (5.20 ± 0.03 ‰) even though mare basalt whole-rock samples are nearly the same in $\delta^{18}O$ as oceanic basalts on Earth ($\sim$5.6 ‰). Thus, the average fractionation of oxygen isotopes between primitive basalt and zircon is smaller on the Moon [$\Delta^{18}O$(WR-Zrc) = 0.08 ± 0.09 ‰] than on Earth (0.37 ± 0.04 ‰). The smaller fractionations on the Moon suggest higher temperatures of zircon crystallization in lunar magmas and are consistent with higher [Ti] in lunar zircons. Phase equilibria estimates also indicate high temperatures for lunar magmas, but not specifically for evolved zircon-forming melts. If the solidus temperature of a given magma is a function of its water content, then so is the crystallization temperature of any zircon forming in that melt. The systematic nature of O and Ti data for lunar zircons suggests a model based on the following observations. Many of the analyzed lunar zircons are likely from K, rare earth elements, P (KREEP)-Zr-rich magmas. Zircon does not saturate in normal mafic magmas; igneous zircons in mafic rocks are typically late and formed in the last most evolved portion of melts. Even if initial bulk water content is moderately low, the late zircon-forming melt can concentrate water locally. In general, water lowers crystallization temperatures, in which case late igneous zircon can form at significantly lower temperatures than the solidus inferred for a bulk-rock composition. Although lunar basalts could readily lose H_2 to space during eruption, lowering water fugacity; the morphology, large size, and presence in plutonic rocks suggest that many zircons crystallized at depths that retarded degassing. In this case, the crystallization temperatures of zircons are a sensitive monitor of the water content of the parental magma as well as the evolved zircon-forming melt. If the smaller $\Delta^{18}O$(zircon–mare basalt) values reported here are characteristic of the Moon, then that would suggest that even highly evolved zircon-forming magmas on the Moon crystallized at higher temperature than similar magmas on Earth and that magmas, though not necessarily water-free, were generally drier on the Moon.

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Introduction

Zircon is a common accessory mineral in evolved igneous rocks from Earth. A range of geochemical information is derived from oxygen isotope ratios ($\delta^{18}O$) and trace element compositions in terrestrial zircons, including temperature of crystallization and compositions of magma sources (Valley 2003; Hanchar and Hoskin 2003; Watson and Harrison 2005; Ferry and Watson 2007). Zircons have also been found in mafic and felsic rocks from the Moon and dated at 4.4–3.9 Ga (Lovering and Wark 1974; Ireland and Wlotzka 1992; Wopenka et al. 1996; Meyer et al. 1996; Grange et al. 2009; Nemchin et al. 2012), and oxygen isotope ratios have been measured in lunar rocks and minerals (Onuma et al. 1970; Wiechert et al. 2001; Clayton 2007; Spicuzza et al. 2007; Liu et al. 2010; Hallis et al. 2010).

Relatively few zircons have been analyzed from the Moon. All but one lunar zircon previously analyzed for $\delta^{18}O$ came from a single Apollo 14 lunar breccia (Nemchin et al. 2006a, b; Whitehouse and Nemchin 2009), and no zircons have been analyzed previously for both $\delta^{18}O$ and [Ti] (Taylor et al. 2009). We report values of both $\delta^{18}O$ and [Ti] from single zircons from four Apollo landing sites with an emphasis on zircons from the lunar regolith. Although the effects of shock on regolith zircon are poorly understood, the Apollo samples of lunar soil contain many zircons amenable to in situ analysis and are an underappreciated resource that may include zircons from parent lithologies not yet recognized in the Apollo rock suite.

Lunar magmas have long been believed to be essentially dry due to early outgassing (Canup 2004; Lucey et al. 2006; Shearer et al. 2006; Sharp et al. 2013). Recently, this conclusion has been re-evaluated based on both remote sensing of H_2, H_2O, and OH on the Moon's surface, and on results from new analytical approaches for lunar samples. A wide range of water contents has been proposed (Saal et al. 2008, 2013; Boyce et al. 2010; Sharp et al. 2010, 2013; McCubbin et al. 2010, 2011, 2012; Greenwood et al. 2011; Elkins-Tanton and Grove 2011; Hauri et al. 2011; Liu et al. 2012a, b; Hui et al. 2013; Tartèse et al. 2013; Barnes et al. 2013). At one extreme, lunar magmas are estimated to be "essentially anhydrous" with [H] lower on the Moon than on Earth by 4–5 orders of magnitude based on a wide 25 ‰ range of Cl isotope ratios. These results suggest that low fH$_2$ stabilized metal chlorides rather than HCl (Sharp et al. 2010, 2013). At the other extreme, analysis of glass inclusions in olivine crystals associated with Ti-rich "orange glass" from Apollo 17 sample 74220 yields 615–1,410 ppm H_2O correlated with [F], [Cl], and [S], leading to the proposal that the volatile content of the sources of lunar magmas was the same as that in Earth's upper mantle and that primitive lunar magmas were similar in water content to terrestrial mid-ocean ridge basalts (Hauri et al. 2011; Saal et al. 2013). Lunar apatites are reported to contain from 0 to 14,000 ppm H_2O leading to estimates of water composition in lunar source regions ranging from <1 to 100 % of that in the Earth's mantle (McCubbin et al. 2010, 2011; Greenwood et al. 2011; Boyce et al. 2010; Tartèse et al. 2013; Barnes et al. 2013). Likewise, high water content is estimated from concentrations of up to 10 ppm in nominally anhydrous minerals from lunar anorthosites (Hui et al. 2013). If correct, these estimates indicate high water fugacities in magma source regions and thus a greater role for near-surface degassing after formation of the lunar magma ocean. As a late crystallizing phase in highly evolved magmas, zircons can provide independent evidence of magmatic conditions, including water content.

The goals of this study are as follows: (1) to evaluate lunar soil as a repository of widely sourced zircons appropriate for petrologic study; (2) to evaluate the geochemical signature of zircons from the Moon versus from Earth; (3) to compare lunar and terrestrial zircons in order to constrain temperatures for crystallization of zircons; and (4) to explore these results as a possible guide to the water content of the parent magmas. Although the number of zircons in Apollo samples made available for this study was small, we hope these results will help guide future work.

Methods and samples

The zircons for this study were separated from samples of four Apollo landing sites in an effort to sample the Moon as broadly as possible. Some of these zircons are from identifiable parent rocks, but many were found as loose grains in lunar soil.

Eighteen zircons are reported here that were suitable for in situ analysis with a 10-μm spot (grains >15 μm diameter; relatively free of cracks and inclusions). These zircons were extracted from Apollo 12 and 14 soil (<1 mm regolith), an Apollo 15 quartz monzodiorite clast (15405), an Apollo 15 breccia with norite (15455), and an Apollo 17 impact-melt breccia (73235) (Fig. 1; Table 1). Eleven zircons were separated from 20 g of soil by handpicking under UV illumination, which causes zircons to luminesce (von Knorring and Hornung 1961; Taylor et al. 2009; Spicuzza et al. 2011). Samples were processed in a laminar flow hood to prevent contamination. After handpicking, the soil samples were put in heavy liquids and only one additional zircon was found. While labor intensive, handpicking yielded some zircons adhering to small fragments of rock that would not have been isolated by normal gravimetric or magnetic techniques unless samples were destructively disaggregated by

Fig. 1 **a** Cathodoluminescence (CL) and **b** back-scattered electron (BSE) images by SEM of lunar zircons from rocks and regolith (Table 1). All images are at the same scale. The locations of SIMS analysis pits are shown in (**b**) along with values of $\delta^{18}O$ (*black ovals*, values rounded to 0.1 ‰) and of [Ti] (*white ovals*, integer values of ppm). Irregular pits are not labeled (see ESM-1 and ESM-2)
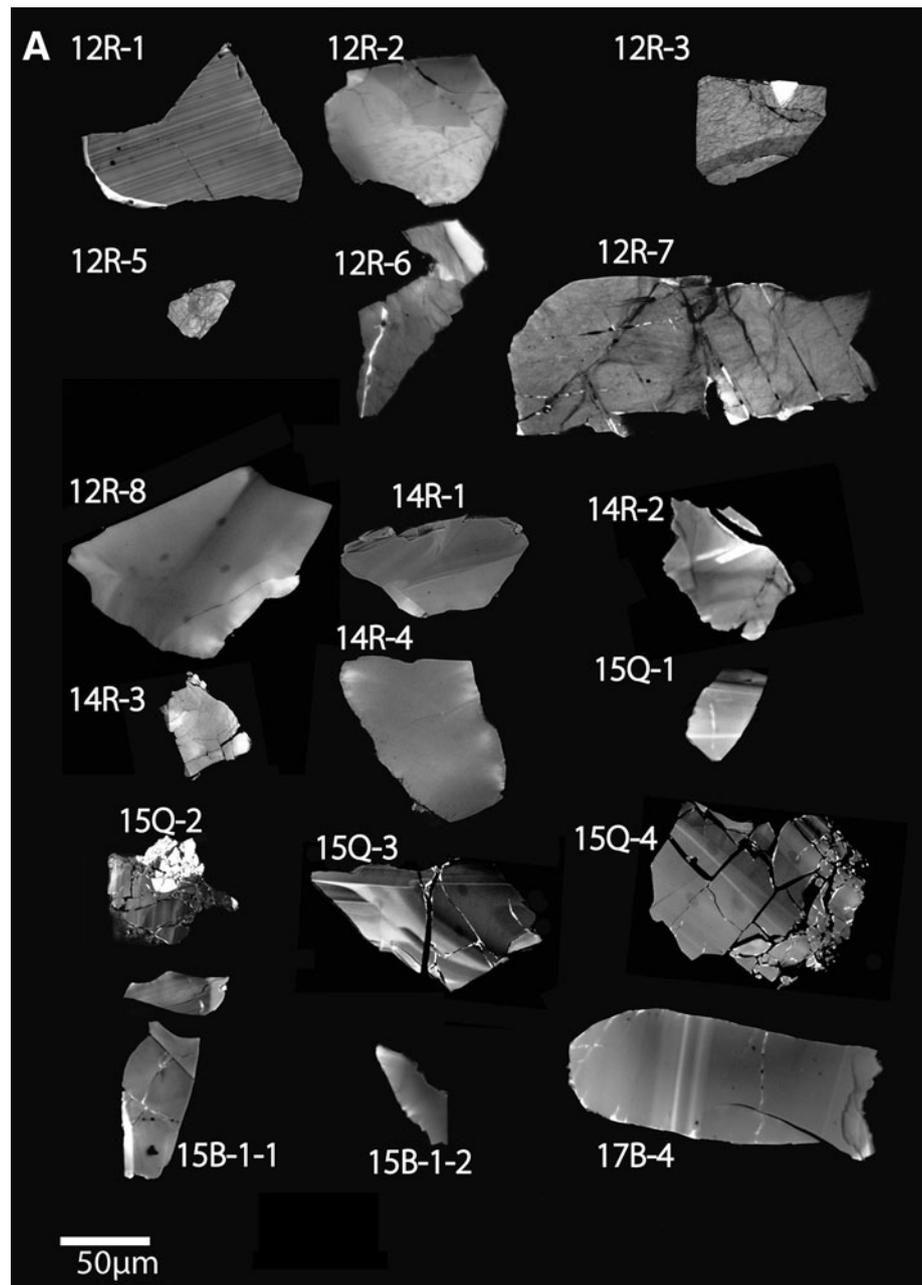

grinding or acid. The mineral assemblages of such samples can provide important information to the compositions of the parent magma.

If the zircon yield from nondestructive separation (handpicking, heavy liquids) is taken as representative of other samples of soil, then the >50 kg of soil collected from the Moon contains 10^4–10^5 zircons that are >15 μm in diameter. This range is probably an underestimate as significant numbers of zircons could be hidden from view within small fragments of rock or glass. Destructive techniques such as grinding or dissolution in HF would readily evaluate this possibility. Clearly, the fine-grained regolith sampled by the Apollo missions represents an important,

previously untapped reservoir of zircon-bearing material from which to study the petrology and geochemistry of known and unknown igneous rocks across both sides of the Moon and possibly elsewhere.

The separated zircons were cast, one zircon per mount, in the center of 25 mm epoxy rounds with the KIM-5 zircon (Valley 2003) and UWQ-1 quartz (Kelly et al. 2007) standards, ground to the optimum depth, polished, and imaged by scanning electron microscope (SEM). Oxygen isotope ratios and trace element compositions were measured in situ from ∼10 μm spots by CAMECA ims-1280 ion microprobe (SIMS, secondary ion mass spectrometer) at the WiscSIMS Laboratory, University of Wisconsin.

Fig. 1 continued
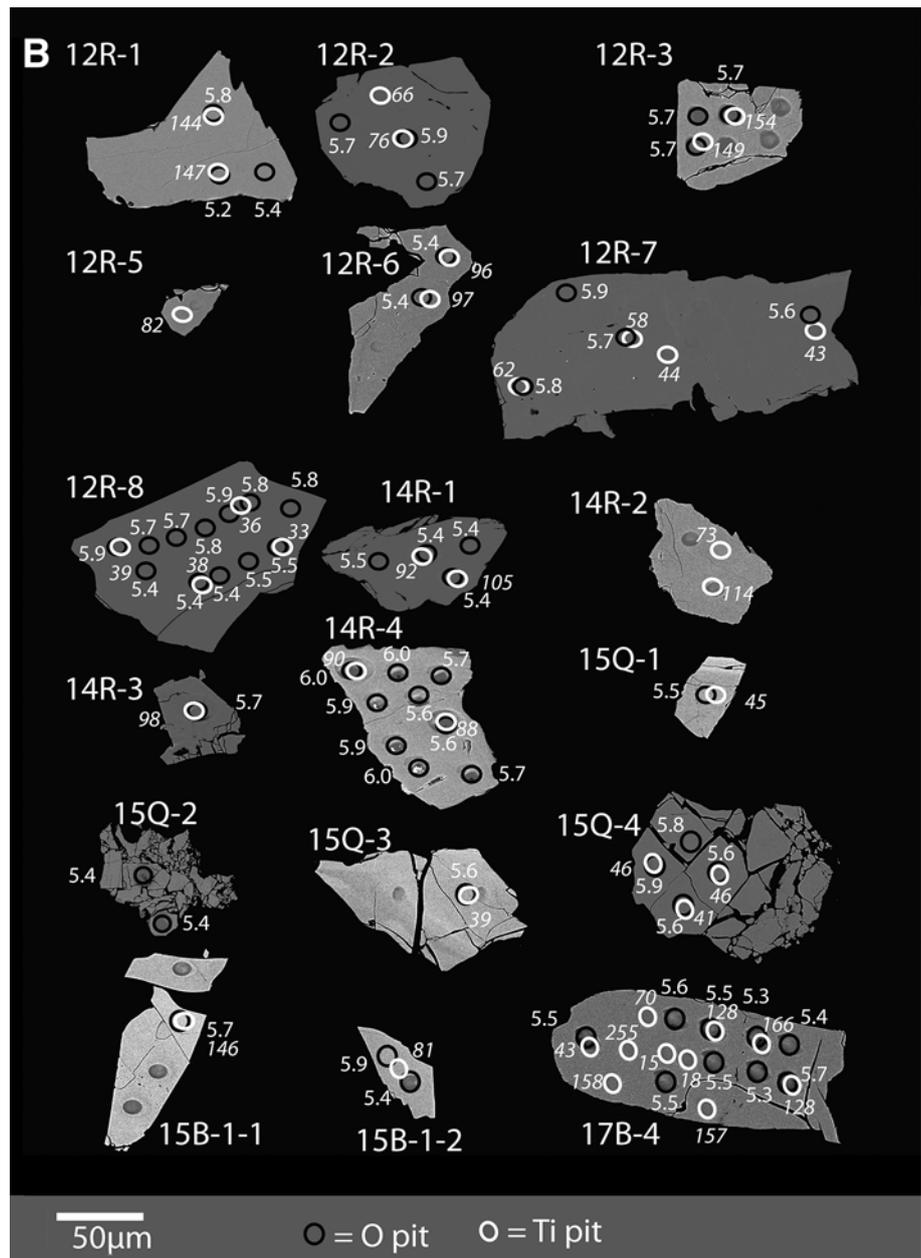
Analysis protocols for $\delta^{18}O$ in lunar zircons closely followed those described elsewhere (Kita et al. 2009; Valley and Kita 2009). During three separate analysis sessions, a $^{133}Cs^+$ primary beam (20 kV total impact voltage, ~ 2.1 nA) was focused on the sample surface; beam diameters for the three sessions were ~ 10 μm (10, 12, 10×14 μm, respectively). Secondary O^- ions were accelerated from the sample, which was at -10 kV. A 40-nm gold coat and a normal-incidence electron gun were used for charge compensation. The intensity of $^{16}O^-$ ions was $\sim 2.6 \times 10^9$ cps, depending on the primary beam intensity ($\sim 1.2 \times 10^9$ cps/nA). Mass resolving power was set to 2,500 (M/ΔM), sufficient to separate hydride interferences

on ^{18}O. Two multi-collector Faraday cups (FC) were used for simultaneous measurement of the $^{16}O^-$ and $^{18}O^-$ signals. The baseline of the FC amplifiers was calibrated at the beginning of each analysis session. Total analytical time per spot was about 4 min, including time for pre-sputtering (10 s), automatic retuning of the secondary ion beam (60 s), and analysis (80 s). A total of eight bracketing analyses of KIM-5 zircon standard ($\delta^{18}O = 5.09$ ‰ VSMOW; Valley 2003), embedded in each sample mount, were used to calibrate the $\delta^{18}O$ analyses of lunar zircons. The average precision for groups of eight bracketing standard analyses is 0.3 ‰ (2 standard deviations, SD), and the average standard error of the mean is 0.1 ‰ (2 SE) (ESM 1).

Table 1 Zircons from lunar soil and rocks

Sample number	Zircon number	Rock type	$\delta^{18}O$ ‰ VSMOW average	Number of spots	[Ti] ppm ave.	Number spots
12023,1	12R-1	Regolith	5.49	3	146	2
12023,1	12R-2	Regolith	5.76	3	71	2
12023,1	12R-3	Regolith	5.69	3	151	2
12023,1	12R-5	Regolith	–	0	82	1
12023,1	12R-6	Regolith	5.41	2	96	2
12023,1	12R-7	Regolith	5.75	4	52	4
12023,1	12R-8	Regolith	5.64	12	36	4
14240,1	14R-1	Regolith	5.41	4	99	2
14240,1	14R-2	Regolith	–	0	93	2
14240,1	14R-3	Regolith	5.73	1	98	1
14240,80	14R-4	Regolith	5.82	9	89	2
15405,217	15Q-1	QMD	5.53	1	45	1
15405,217	15Q-2	QMD	5.43	2	–	0
15405,217	15Q-3	QMD	5.55	1	39	1
15405,217	15Q-4	QMD	5.70	4	44	3
15455,55	15B-1	Breccia	5.65	1	146	1
15455,55	15B-2	Breccia	5.64	2	81	1
73235,87	17B-4	Breccia	5.48	9	$(114)^2$	10
		Ave.	5.61			
		2 SE	0.07			

Values of $\delta^{18}O$ and [Ti] measured in situ from 10 μm spots by ion microprobe at WiscSIMS

Sample number prefixes (12, 14, 15, and 7) denote Apollo 12, 14, 15, and 17, respectively

QMD quartz monzodiorite

$(114)^2$ = heterogeneously disturbed zircon with [Ti] = 15–255 ppm

After analysis, all pits were examined by SEM. A total of 61 analyses are regular in appearance, and 18 pits are "irregular" (13 are on cracks, 5 overlap adjacent phases or an inclusion). Oxygen isotope analyses from irregular pits are often less precise and sometimes inaccurate (Cavosie et al. 2005; Kita et al. 2009; Spicuzza et al. 2011). While the average $\delta^{18}O$ of the 18 analyses from irregular pits (5.45 ‰) is indistinguishable from the average for the 61 regular analyses (5.61 ‰), the variability of the irregular analyses is greater due to one irregular analysis above 6.2 and four below 5.1 ‰. As in other studies, we have judged all analyses from pits that are irregular in appearance by SEM as unreliable regardless of the measured $\delta^{18}O$ value. All data are reported in ESM 1, and irregular pits are identified.

Titanium abundances in the lunar zircons were measured during two sessions using the axial electron multiplier and magnetic peak switching. Analysis protocols were similar to those for the trace element analyses reported by Page et al. (2007). A $^{16}O^-$ primary beam (23 kV total impact voltage) was focused to ∼10 μm (10 μm diameter with an intensity of 1.7 nA for session 2, and 14 × 20 μm with an intensity of 4.5 nA for session 1) on the sample surface, and positive secondary ions were accelerated by 10 kV. A 40-volt energy offset was applied. Mass resolving power was set to 4,000. For lunar zircons, both $^{49}Ti^+$ ion and $^{30}Si^+$ ions were measured and the $^{49}Ti^+/^{30}Si^+$ ratio was used to calculate Ti concentration. The NIST 610 glass (434 ppm Ti; Pearce et al. 2007) was measured as a running standard. Use of an energy offset virtually eliminates the matrix-related difference in Ti sensitivity between zircon and the NIST 610 glass standard (data from Page et al. 2007), so that the relative sensitivity factor (RSF = $(^{49}Ti^+/^{30}Si^+)/(Ti, ppm/Si, wt\%))$ calculated from NIST 610 glass could be applied to calculate the Ti concentrations in the zircons. After analysis, SIMS pits were examined by SEM. Forty-one pits are regular in appearance, and one overlaps a glass-filled fracture and is not considered reliable. All Ti data are shown in ESM 2.

Results

A total of 61 spots were analyzed in 16 zircons for $\delta^{18}O$ (Fig. 2a; Table 1). Previous studies of the Moon have shown that oxygen isotope fractionations are mass-dependent and that values of $\Delta^{17}O$ (=$\delta^{17}O$–0.52 $\delta^{18}O$) are identical to those on Earth within ±0.01 ‰ (Wiechert et al. 2001; Spicuzza et al. 2007; Hallis et al. 2010), and thus, ^{17}O was not measured in the zircons. An additional 41 spots were analyzed for Ti (Table 1).

In spite of the large range of sample localities and potential parent rock types, the oxygen isotope ratios of all lunar zircons analyzed thus far are remarkably constant both within single grains and from sample to sample (Fig. 2a). The analytical precision of $\delta^{18}O$ analyses in this study is a factor of 2 better than in other studies of lunar zircons, and

Fig. 2 Histograms of oxygen isotope ratio for zircons and basaltic whole rock from the Moon (*red*) and Earth (*green*). **a** $\delta^{18}O$ of lunar zircons. **b** $\delta^{18}O$ of whole-rock samples of Mare basalt. **c** $\delta^{18}O$ of terrestrial zircons from oceanic crust. **d** $\delta^{18}O$ of mid-ocean ridge basalts (MORB) from the Indian, Atlantic, and Pacific oceans, and the Australian–Antarctic discordance. Values for zircon were measured in situ by SIMS (Moon: this study; Nemchin et al. 2006a; Whitehouse and Nemchin 2009. Earth: Grimes et al. 2011). WR compositions for basalts were measured by laser fluorination (Moon: Spicuzza et al. 2007; Liu et al. 2010; Hallis et al. 2010. MORB: Cooper et al. 2009)
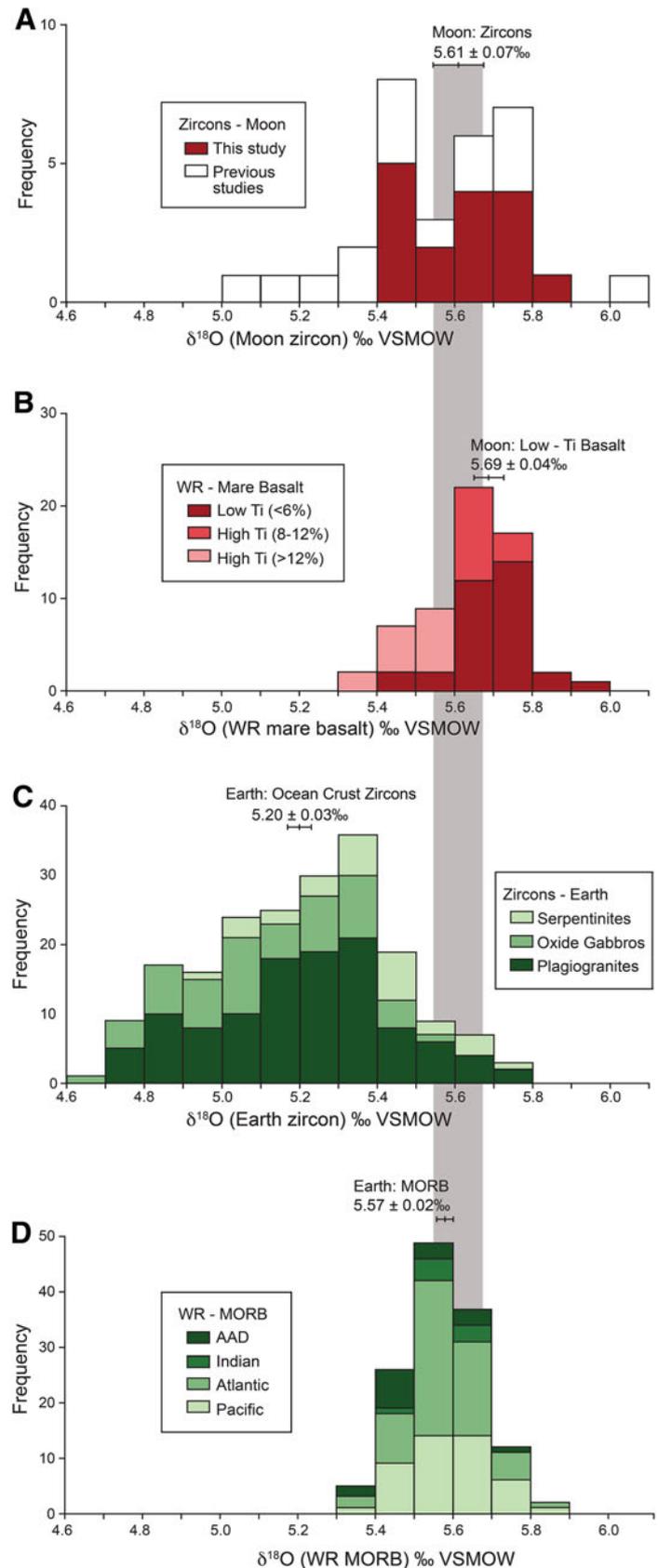
all grains are homogeneous in $\delta^{18}O$ within the reproducibility of single analyses for our data (2 SD = 0.3 ‰). Likewise, previous SIMS data for lunar zircons are homogeneous within the single-spot precision of those studies (2 SD = 0.6 ‰) for samples that were prepared without sample relief (Kita et al. 2009; Whitehouse and Nemchin 2009; Valley and Kita 2009). In this study, the measured $\delta^{18}O$ values for six zircons are separated from Apollo 12 soil average 5.65 ± 0.10 ‰ (2 SE). We report two standard errors of the mean (2 SE) for average values and two standard deviations (2 SD) for single analyses. Three Apollo 14 soil zircons also average 5.65 ± 0.25 ‰, and four zircons from Apollo 15 quartz monzodiorite average 5.56 ± 0.11 ‰. The average values for all 16 zircons of this study average $\delta^{18}O$ = 5.61 ± 0.07 ‰ (2 SE), in good agreement with 15 published analyses of lunar zircons (5.52 ± 0.13 ‰ 2 SE) (Nemchin et al. 2006a, b; Whitehouse and Nemchin 2009) (Fig. 2a). Thus, all analyzed lunar zircons have identically the same value of $\delta^{18}O$ within analytical uncertainty. This small range in measured $\delta^{18}O$ values and the excellent precision is the same as that attained for a comparable number of analyses on a homogeneous standard in these studies, and no correlations are found with location, parent rock type, or indications of fracture or shock deformation (Spicuzza et al. 2011).

The intra-grain values of [Ti] in lunar zircons from this study typically differ by less than 10 ppm, but grain-to-grain they range from 36 to 146 ppm (Fig. 3a; Table 1). For instance, three zircons from quartz monzodiorite average 43 ppm and range from 39 to 45. One anomalous zircon grain from an impact-melt breccia (73235, 17B-4 in Fig. 1) yielded a wide range of values from 15 to 255 ppm Ti with no discernible pattern of zoning and is interpreted to be disturbed and not preserve the primary magmatic Ti composition. Grange et al. (2009, 2011) report [Ti] data for shocked zircons from breccia 73235, and anomalously high (>500 ppm Ti) and variable [Ti] in zircons from breccia 73217. These values are too high for magmatic zircons (Watson and Harrison 2005). Some analyses might include intergrowths of other minerals, and some may also be disturbed zircon. The undisturbed inclusion-free [Ti] values from this study are lower and consistent with the range reported for 27 zircons from Apollo 14 polymict breccias (58–260 ppm) by Taylor et al. (2009). Taken together, the undisturbed lunar zircons are Ti-rich and vary from 36 to 260 ppm Ti (Fig. 3a).

Discussion

The lunar magma ocean model (LMO) posits that the Moon consists of a plagioclase-rich crust overlying a ~400-km-thick ultramafic cumulate pile (Wood et al. 1970; Lucey et al. 2006; Shearer et al. 2006; Wieczorek

Fig. 3 Ti compositions (ppm, wt.) in zircons from the Moon and Earth, and model Ti-in-zircon temperatures calculated with no corrections for reduced activity or pressure, see text. **a** Lunar zircons (this study, Taylor et al. 2009). Terrestrial values for: **b** felsic to intermediate plutonic rocks (Fu et al. 2008), **c** rhyolites (Fu et al. 2008), **d** mafic plutonic rocks (Fu et al. 2008), and **e** kimberlite megacrysts (Page et al. 2007)
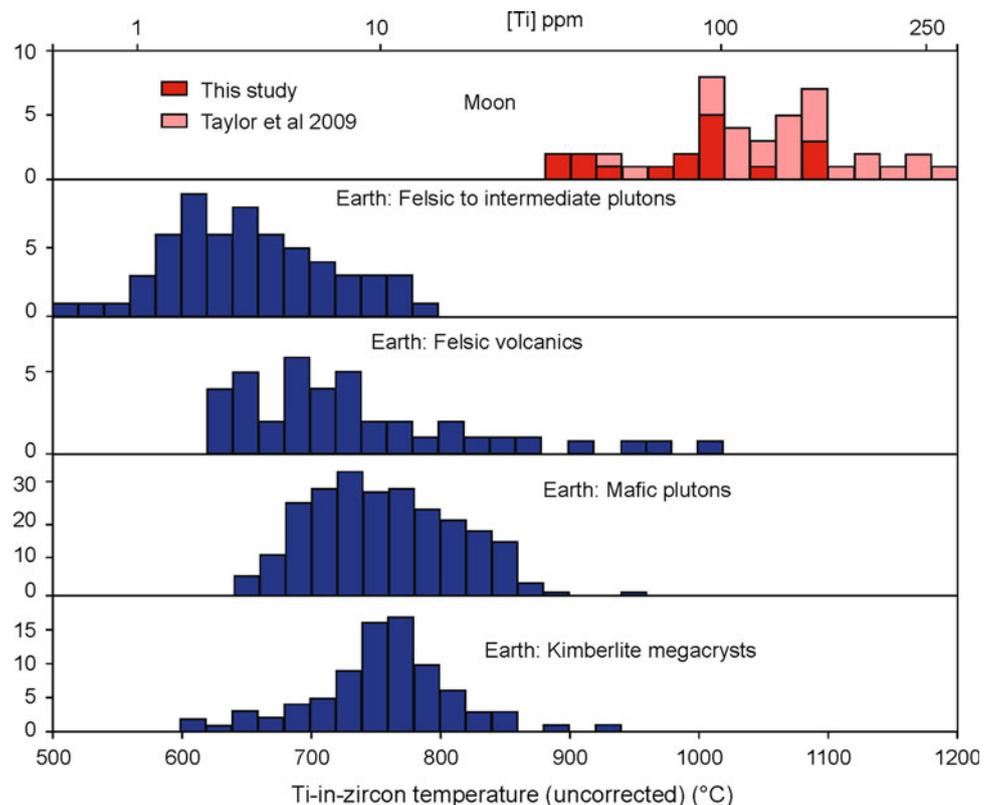
et al. 2006). Late-stage ilmenite-rich differentiates are thought to have been heterogeneously reintroduced to the cumulate pile due to gravitational instability (Ringwood and Kesson 1976; Spera 1992). The last LMO liquids to crystallize are incompatible-element-enriched and referred to as KREEP (K, rare earth elements, P) (Warren 1985). Trapped, intercumulus liquids in upper mantle cumulates would also be incompatible-element-enriched, resembling KREEP (Snyder et al. 1995; Wieczorek et al. 2006). Water, as an incompatible component, should also be concentrated in KREEP during the crystallization of the LMO. Crystallization of lunar igneous zircon required such an incompatible-element-rich (including Zr) KREEP component in the source (or as an assimilant). Although the post-LMO lunar mantle is stratified chemically, evidence suggests that high-temperature equilibration with respect to oxygen isotopes was maintained (Spicuzza et al. 2007). Magmas derived from the lunar mantle produced mare basalts (Shearer et al. 2006) and zircon-bearing lithologies.

Zircons in lunar regolith

Most zircons separated from the lunar soil occur as individual crystals, and thus, their host rock is not known. Potential sources include parent rocks that varied in composition from mafic to felsic granophyre, including intrusive and extrusive magmas, and impact melts. The lunar regolith is dominated by shocked rock, breccias, mineral fragments, and impact-related melts. Some lunar zircons show certain features, including anomalous trace element compositions, reset U–Pb ages, and micro-twin lamellae that indicate they experienced impact (Nemchin et al. 2010; Pidgeon et al. 2011; Spicuzza et al. 2011; Timms et al. 2012; Grange et al. 2013). Zircons could also have crystallized from impact melts and be shocked or unshocked.

It is reasonable to consider if a high percentage of lunar regolith zircons formed by crystallization of impact melts. On Earth, large impacts on felsic target rocks can form melt sheets that crystallize zircon. Such zircons might be isotopically or chemically distinct from other igneous zircons, although studies from terrestrial impact melts suggest that trace element differences are subtle (Wielicki et al. 2012a). However, the high temperatures and high [Zr] necessary to saturate zircon in mafic magmas make impact-melt zircons unlikely to be a significant proportion of zircons on the Moon where there are no significant felsic or intermediate-composition target rocks (Dickinson and Hess 1982; Watson and Harrison 1983; Wielicki et al. 2012a, b). Furthermore, terrestrial impact-melt zircons have only mildly elevated [Ti] relative to Archean or Hadean zircons on Earth; they are significantly lower in [Ti] than zircons from the Moon (Fu et al. 2008; Wielicki et al. 2012a, b);

and impact-related processes alone do not explain the geochemistry of lunar zircons.

Since the majority of the lunar soil is derived from local bedrock (Papike and Shearer 1998), zircons from Apollo 12, 15, and 17 are likely of different parentage than the previously studied Apollo 14 breccia zircons (Nemchin et al. 2010; Grange et al. 2011) and expand the lunar zircon suite for the Moon. Apollo 14 impact breccia zircons tend to show strong provinciality in composition and apparently in parent rock type (Nemchin et al. 2010; Grange et al. 2011; Liu et al. 2012a, b), but it is still possible that some soil zircons came from long distances, outside the limited area sampled by the Apollo missions. A larger study of regolith zircons (and lunar meteorites) would potentially extend the zircon suite to include lunar lithologies not represented in the Apollo and Luna rock and breccia suites. It is also likely that the lunar regolith contains zircons derived from other planetary bodies, including the early Earth (Armstrong et al. 2002). Although the chances of finding exotic far-travelled zircons are remote in the small sample suites studied to date, a large number of unstudied zircons exist in Apollo sample collection.

Oxygen isotopes

Previous studies have shown that lunar igneous rocks preserve high-temperature equilibrated oxygen isotope ratios, as would be expected for magmas differentiated from a well-mixed source such as the lunar magma ocean and its remelted derivatives (Wiechert et al. 2001; Spicuzza et al. 2007; Liu et al. 2010; Hallis et al. 2010). If correct, then both the mare basalt and zircon-bearing magmas were derived from a lunar mantle source with oxygen isotope ratios that equilibrated at magmatic temperatures. This assumption underlies our model that compares the $\delta^{18}O$ values of lunar igneous zircon, irrespective of parent rock, to values for olivine (Ol) and whole rock (WR) from mare basalts. The fact that all lunar zircons in this study have indistinguishable values of $\delta^{18}O$ provides strong support for this model. We note, however, that such a simplifying assumption would not be appropriate on Earth where the combined effects of plate tectonics and a hydrosphere have resulted in much greater fractionation of oxygen isotopes. Zircons from different sources on Earth commonly range by 5–10 ‰ in $\delta^{18}O$, and extreme values vary by over 50 ‰ (Valley et al. 2005; Cavosie et al. 2011; Bindeman and Serebryakov 2011). It is significant that such variability of $\delta^{18}O$ (Zrc) has not been found on the Moon.

The interpretation of lunar data can be simplified by comparing $\delta^{18}O$ of zircons to $\delta^{18}O$ for model basalt with constant composition. In this case, the fractionation of oxygen isotopes between zircons and basalt reflects the temperature of crystallization of zircon. On the Moon, this

comparison is valid as long as the zircon-forming melts were all in high-temperature oxygen isotope equilibrium, even for regolith zircons where the parent rock is not available for analysis. This also applies to shocked zircons, which, in the absence of water, will not be altered in $\delta^{18}O$ (Spicuzza et al. 2011). It is not required that these phases all coexisted in the same rock or the same melt for oxygen isotope ratios to reflect equilibration at magmatic temperatures with an original parent composition (Valley et al. 1994). This model is supported by the constant values of $\delta^{18}O(Zrc)$ and $\delta^{18}O(Ol)$ on the Moon even though the $\delta^{18}O(WR)$ values for mare basalts vary systematically with Mg, Ti, and other elements reflecting an equilibrated source (Spicuzza et al. 2007).

The correlations of $\delta^{18}O(WR)$ with major element chemistry shown in Fig. 4a, b reflect changes in modal mineralogy resulting from different or evolving bulk-rock compositions. It is important to note that $\delta^{18}O$ for a mineral, such as olivine or zircon, remains nearly constant because the value of $\Delta^{18}O(WR\text{-mineral})$ varies at the same rate as $\delta^{18}O(WR)$ for closed-system, isothermal fractional crystallization (Valley 2003; Lackey et al. 2008). If WR composition is constant, then variable temperature has a very small effect on $\delta^{18}O(Zrc)$ and a larger effect on $\Delta^{18}O(WR\text{-Zrc})$ because the fractionations are small. If WR composition varies, relatively larger changes are seen for values of $\Delta^{18}O(WR\text{-Zrc})$ and $\Delta^{18}O(WR\text{-Ol})$ as a result of changing mineral modes, but the $\delta^{18}O$ of each mineral is
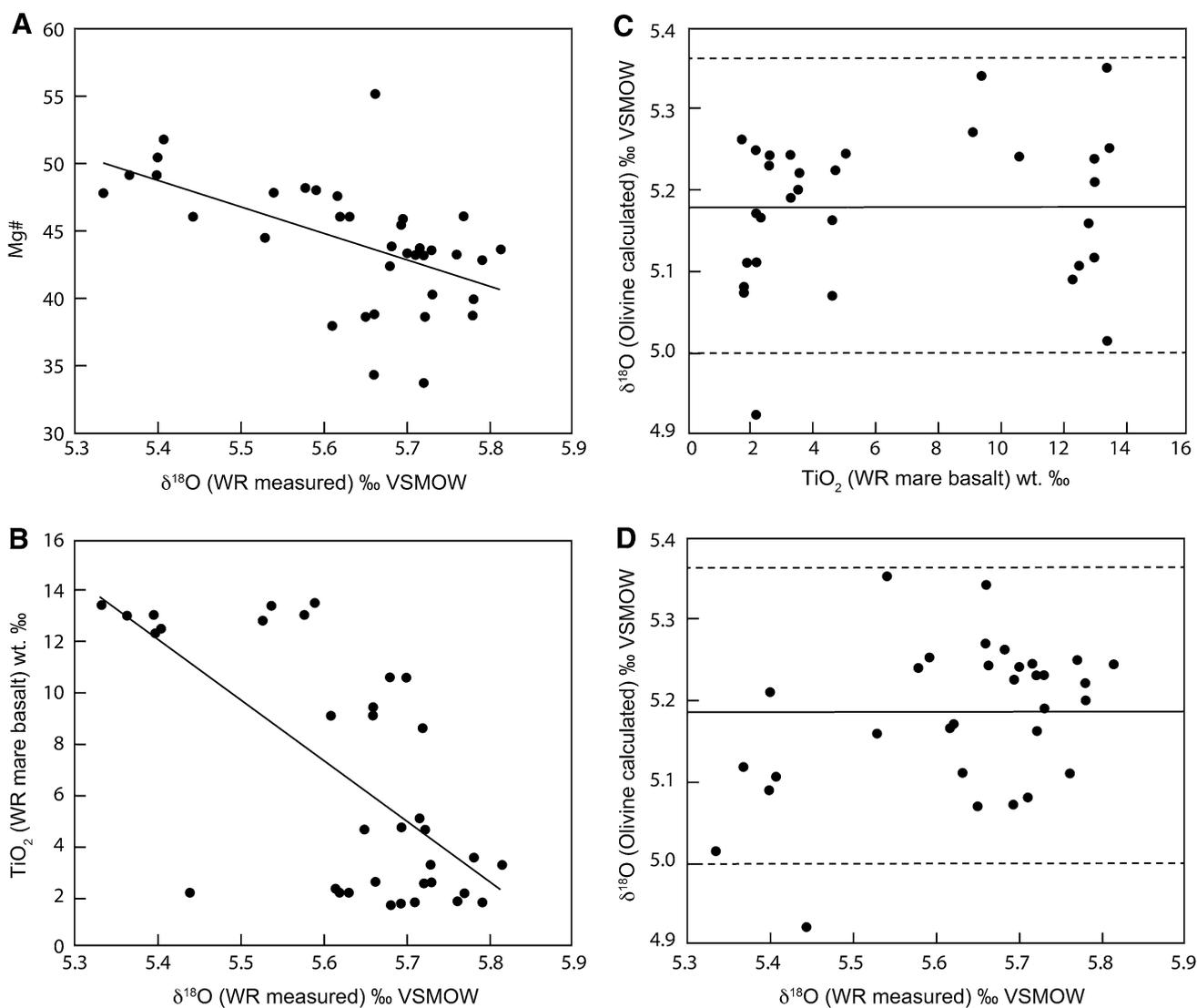

Fig. 4 **a** and **b** plots of Mg# and wt% TiO_2 for mare basalts versus measured $\delta^{18}O$ for whole-rock samples showing small systematic changes in $\delta^{18}O(WR)$ resulting from different magma composition and mineralogy. **c** and **d** show the calculated $\delta^{18}O$ value of lunar olivine versus measured wt% TiO_2 and $\delta^{18}O(WR)$. The constant $\delta^{18}O(Ol)$ value of 5.18 ± 0.18 ‰ (2 SD, 2 SE = 0.03) is calculated at 1,200 °C based on mineralogy estimated from WR chemistry (Spicuzza et al. 2007). *Dashed lines* are at ±2 SD

nearly invariant (Valley 2003; Lackey et al. 2008). This is illustrated in Fig. 2b, which divides mare basalts into three groups based on Ti showing that high-Ti basalts have systematically lower values of $\delta^{18}O(WR)$. Likewise, Fig. 4b plots wt% TiO_2 to show the correlation with $\delta^{18}O(WR)$. In both figures, the $\delta^{18}O(WR)$ values of low-Ti basalts (<6 wt% TiO_2) average 5.69 ± 0.04 ‰ (2 SE); high-Ti basalts with 8–12 % Ti average 5.66 ± 0.02 ‰; and high-Ti basalts with >12 % Ti average 5.48 ± 0.04 ‰ (Spicuzza et al. 2007; Liu et al. 2010; Hallis et al. 2010). The volumetrically dominant low-Ti basalts have higher $\delta^{18}O(WR)$ than high-Ti basalts merely because the higher abundance of low-$\delta^{18}O$ minerals such as ilmenite lowers the bulk $\delta^{18}O$ of high-Ti magmas. These small differences are predicted for melts that equilibrated at high temperature (Spicuzza et al. 2007), but the $\delta^{18}O$ values of zircon (Fig. 2a) and Ol (Fig. 4c, d) do not vary.

The calculated $\delta^{18}O(Ol)$ in high-temperature equilibrium with both high- and low-Ti mare basalt is exactly the same (5.18 ‰, Fig. 4c, d). Spicuzza et al. (2007) discussed the reasons that this is predicted even though values of $\delta^{18}O(WR)$ vary. Calculated $\delta^{18}O(Ol)$ values are independent of wt% TiO_2 and magmatic differentiation in general because differences in $\delta^{18}O(WR)$ are matched by the changes in modal mineralogy and $\Delta^{18}O(WR-Ol)$, such that the $\delta^{18}O(Ol)$ value is constant in spite of small changes in $\delta^{18}O(WR)$ (Fig. 4d). Likewise, mare basalts and lunar zircon-producing magmas are derived from an oxygen-isotope-equilibrated mantle source, namely LMO cumulates (Onuma et al. 1970; Lucey et al. 2006; Spicuzza et al. 2007; Liu et al. 2010; Elkins-Tanton and Grove 2011). At equilibrium, the magma–zircon fractionation of $\delta^{18}O$ is small for any given magma composition, but during fractional crystallization, the value of $\delta^{18}O(WR)$ varies as a function of changing major element concentrations that produce the differences in modal mineralogy (Valley 2003), while $\delta^{18}O(Ol)$ remains constant.

Like olivine, the calculated $\delta^{18}O$ of zircon is the same for lunar magmas of different whole-rock (WR) composition. This prediction is consistent with the oxygen isotope data for lunar zircons. Within analytical uncertainty, all $\delta^{18}O$ measurements in zircons in this study have the same value of $\delta^{18}O$ (5.61 ± 0.07 ‰, Fig. 2a). All previously published $\delta^{18}O$ values are also consistent with this average value (Nemchin et al. 2006a; Whitehouse and Nemchin 2009). The comparison of $\delta^{18}O$ in low-Ti mare basalts to $\delta^{18}O$ in zircons yields a precisely determined value of $\Delta^{18}O(WR-Zrc) = 0.08 \pm 0.09$ ‰. Furthermore, the average values of $\delta^{18}O$ for lunar zircon (5.61 ‰) and Ol (5.18 ‰) correspond to $\Delta^{18}O(Ol-Zrc) = -0.43$ ‰ and a temperature of $\sim 1{,}200 \pm 150$ °C (Valley 2003), supporting the model that zircon and olivine retain high-temperature equilibrium with an equilibrated high-temperature mantle reservoir, even

though they may have been crystallized in different magmas. In detail, only a large variation in temperature during crystallization could change this prediction, as will be discussed after presentation of results for [Ti]. It is a significant difference that on Earth, values of $\Delta^{18}O(Ol-Zrc)$ from oceanic crust are close to 0 ‰ and are not in equilibrium (Valley 2003). This likely reflects the later crystallization of hydrous zircon-forming melts, and lower temperatures for crystallization of zircon than olivine in terrestrial oceanic crust. The simplifying assumption that on the Moon, values of $\delta^{18}O(Zrc)$ can be compared to $\delta^{18}O(basalt)$, irrespective of parent rock, does not apply to modern Earth and accordingly, we only compare oceanic crust zircons to MORB.

Ti in zircon

The equilibrium Ti content of zircon yields an estimate of crystallization temperature if corrections are made for the activity of SiO_2 and TiO_2, and pressure (Watson and Harrison 2005; Ferry and Watson 2007) and other complications are not significant (nonequilibrium processes, inclusions in zircon, Fu et al. 2008; Hofmann et al. 2009). Although these corrections are uncertain when the composition of the parent magma is unknown, the effects are significantly less than the difference shown in Fig. 3 between Earth and the Moon. For instance, use of αTiO_2 ~ 0.6 as suggested by the presence of ilmenite would add 30–50 °C to temperature estimates; a similar reduction in αSiO_2 would lower the temperature by a comparable amount; and correction for near-surface pressures would decrease temperatures by 50–100 °C (Ferry and Watson 2007; Ferriss et al. 2008). Lower oxygen fugacities on the Moon stabilize Ti^{3+}, but differences in fO_2 have been shown not to affect partitioning of Ti in zircon (Burnham and Berry 2012). Thus, the corrections for Ti-in-zircon thermometry partially cancel each other, and for equilibrium conditions, temperature is the main control of [Ti] in zircon. The large temperature differences between Earth and the Moon suggest different magmatic conditions. The temperatures shown in Fig. 3a for zircons crystallized on the Moon generally compare well to estimates from petrologic and oxygen isotope thermometers for crystallization of lunar magmas (Onuma et al. 1970; Green et al. 1975; Elkins-Tanton et al. 2003; Shearer et al. 2006).

The homogeneity of [Ti] observed in all but one zircon (17B-4) in this study suggests that the bulk of each crystal grew over a relatively narrow temperature range. For instance, the three zircons from a quartz monzodiorite clast were analyzed for a total of 5 times with spot analyses ranging from 39 to 46 ppm Ti (Table EA 2), yielding uncorrected temperatures of 892–913 °C. Two spots on the second most heterogeneous zircon (from regolith 14240) yield 974 and 1,041 °C.

Taken as a whole, values of [Ti] in terrestrial igneous zircons from felsic and mafic rocks are significantly lower, showing almost no overlap with lunar igneous zircons (Fig. 3). The combination of $\delta^{18}O = 5.6$ ‰ and [Ti] >40 ppm is uniquely characteristic as a signature of zircons from the Moon. The difference in [Ti] indicates zircon-producing lunar magmas were 200–400 °C hotter than equivalent zircon-bearing magmas on Earth. It is significant that on Earth, zircon-producing mafic magmas were differentiated and enriched in volatiles.

Lunar versus terrestrial magmas

The values of $\delta^{18}O$ for zircon, like [Ti], contrast between the Moon and Earth. Most significantly, the relatively large 3 ‰ range of $\delta^{18}O(Zrc)$ values in igneous zircons from Archean continental crust on Earth (Valley et al. 2005) is not found in lunar igneous zircons due to the absence of a hydrosphere on the Moon. Magmatic zircons from oceanic crust on Earth are much less variable than those in continental crust and provide a good comparison to lunar zircons. These terrestrial zircons preserve primitive values that are not measurably affected in $\delta^{18}O$ by subsolidus exchange (Cavosie et al. 2009; Grimes et al. 2011; Schmitt et al. 2011).

When $\delta^{18}O$ values of zircons on the Moon are compared to igneous zircons from basaltic magmas and their derivatives in terrestrial oceanic crust, there is a small, but precisely defined difference. Since the magnitude of the differences in $\delta^{18}O$ values in this comparison is small, we compare only data measured using the same techniques and reference standards. Mixing of data sets employing differing techniques or standards could introduce systematic, tenths-of-permil offsets in measured $\delta^{18}O(Zrc)$ or $\delta^{18}O(WR)$. Igneous zircons found in gabbros and plagiogranites from mid-ocean ridge environments in terrestrial oceanic crust yield $\delta^{18}O(Zrc) = 5.20 \pm 0.03$ ‰ (2 SE, $N = 197$) from multiple localities in different ocean basins (Fig. 2c, Cavosie et al. 2009; Grimes et al. 2011). There is no systematic difference among the zircons hosted by these two rock types. Although the host magmas are differentiated from MORB sources and not strictly MORB-like in chemistry, the values of $\delta^{18}O(Zrc)$ are in excellent agreement with other estimates of $\delta^{18}O$ in the Earth's mantle (Mattey et al. 1994; Valley et al. 1998; Eiler 2001; Valley 2003; Page et al. 2007). Grimes et al. (2011) showed that for mid-ocean ridge settings, even in plagiogranites that may form by hydrous partial melting of oceanic crust (Koepke et al. 2007; Wanless et al. 2010), the amounts of aqueous fluid are low and $\delta^{18}O$ of the magmatic source is not detectably affected. Thus, it is significant that the average $\delta^{18}O(Zrc)$ value in oceanic crust is 0.41 ‰ lower than the average value of 5.61 ‰ for all lunar zircons.

The average WR $\delta^{18}O$ value for mid-ocean ridge basalts is 5.57 ‰ (± 0.02, 2 SE; Cooper et al. 2009; normalized to $\delta^{18}O(UWG-2) = 5.80$ ‰). This value is not significantly different from that of MORB whole rocks from the Pacific, Atlantic, or Indian Oceans or from the Australian–Antarctic discordance (Fig. 2d). The MORB average of 5.57 ‰ is close to the value for low-Ti mare basalts (5.69 ‰). Thus, zircons from the Moon are heavier than from Earth, but the $\delta^{18}O$ values for basalt are nearly the same. In other words, the lunar zircons are much less fractionated relative to lunar basalts that are representative of the Moon (mare basalt vs. lunar zircon: $\Delta^{18}O(WR\text{-}Zrc)_{Moon} = 0.08 \pm 0.09$ ‰) than is seen in the closest terrestrial analog (oceanic crust, MORB vs. zircon: $\Delta^{18}O(WR\text{-}Zrc)_{Earth} = 0.37 \pm 0.04$ ‰).

The 0.29 ‰ difference in $\Delta^{18}O(WR\text{-}Zrc)$ between the lunar and terrestrial magmas is most strongly influenced by higher temperatures for crystallization of zircon from lunar magma. There are variations with the major element composition of the melt, but as discussed earlier, this effect is removed by comparing to a melt of constant basaltic composition (Grimes et al. 2011). The temperature coefficient for $\Delta^{18}O(WR\text{-}Zrc)$ is too small for quantitative thermometry (Fig. 5), but the effect of temperature can be approximated from the relation:

$$\Delta^{18}O(WR\text{-}Zrc) \sim 1000 ln\alpha(WR\text{-}Zrc) = A\left(10^6/T^2\right)$$

where A is a constant and T is in K. If the terrestrial value of $\Delta^{18}O(WR\text{-}Zrc) = 0.37 \pm 0.04$ ‰ is assumed to be equilibrated at a temperature of 750 °C, as suggested for zircons in many mafic rocks by Ti-in-zircon (Fig. 3), then $A = 0.39$, and for the same composition melt, the lunar fractionation of 0.08 ± 0.09 ‰ would yield a very high, but imprecise temperature of $1,880 \pm 700$ °C. This large uncertainty results, in part, from the precision of $\Delta^{18}O(WR\text{-}Zrc)$ for the
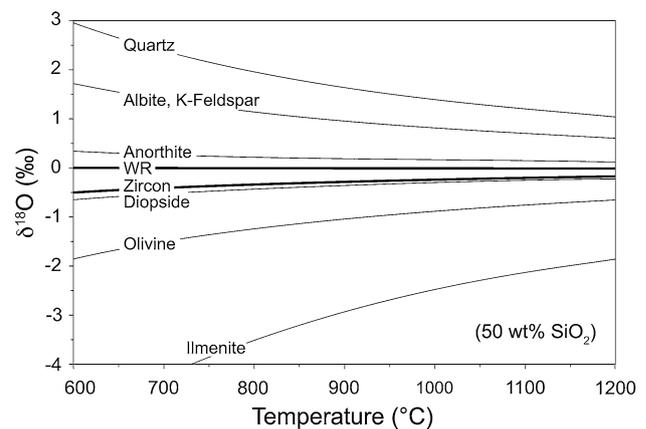

Fig. 5 Fractionation of $\delta^{18}O$ among minerals in isotopic equilibrium with a basalt magma (WR = 50 wt% SiO_2). The fractionation of $\delta^{18}O$ between melt and zircon is 0.2–0.3 ‰ smaller at high temperature

Moon (0.08 ± 0.09 ‰). A more reasonable temperature of 1,240 °C results if $\Delta^{18}O(WR-Zrc) = 0.17$ on the Moon, which is within the 2 SE uncertainties of the lunar SIMS data. Differences in the terrestrial fractionation or the average terrestrial zircon temperature could lower this value further. Thus, although not precisely determined, the oxygen isotope data yield temperature estimates that are consistent with those based on [Ti] for zircons from lunar versus terrestrial magmas. These new zircon $\delta^{18}O$ and [Ti] data support previous conclusions of high solidus temperatures on the Moon, but importantly, they extend this estimate to the differentiated zircon-forming melts.

Because zircons crystallize late, the zircon record includes the latest differentiation history of their respective magmas and adds new information to complement petrologic studies. The last zircons to form in a moderately hydrous mafic magma will crystallize in water-saturated small-volume differentiates at lower temperatures (Dickinson and Hess 1982), which may explain the preponderance of terrestrial zircons that yield Ti-in-zircon temperatures lower than the expected solidus (Fu et al. 2008). In contrast, for a dry magma, the latest melt to crystallize will be at temperatures similar to that of the bulk of the parent rock. Both the $\delta^{18}O$ and [Ti] results suggest that many lunar zircons crystallized from evolved felsic and/or KREEP-rich magmas that were 200–500 °C hotter than terrestrial analogs. The simplest interpretation of these results is that magmas evolved to zircon-forming compositions that crystallized at lower temperatures on Earth than on the Moon and that the primary cause for this difference is the amount of water in the respective magmas.

Water in the Lunar Magma Ocean

The most direct estimates of water content in the lunar magma ocean come from analysis of melt inclusions in olivine, but to date, this has been done from only one sample (Hauri et al. 2011). Data from apatite and the nominally anhydrous minerals, olivine, plagioclase, and pyroxene, yield estimates that range from as high as that from melt inclusions to more than two orders of magnitude lower (McCubbin et al. 2010, 2011, 2012; Greenwood et al. 2011; Tartèse et al. 2013; Hui et al. 2013). However, these estimates are based on uncertain values of the distribution of H_2O between apatite versus melt (Vander Kaaden et al. 2012) and require models that reconstruct the poorly constrained effects of partial melting, fractional crystallization, and diffusive outgassing of hydrogen.

The lunar zircon data do not yield quantitative estimates of water content in the lunar magma ocean, but offer a comparison to Earth. Since evolved melts would have concentrated any water available from their parent magmas (Elkins-Tanton and Grove 2011), the higher temperatures of

zircon-forming magmas on the Moon indicate either that the parent magma was relatively water poor or that it contained water that was lost prior to crystallization of the zircon. If mare basalt magmas were hydrous, diffusive hydrogen loss to space during eruption of basalts would be more rapid on the Moon than Earth because of lower oxygen fugacity and atmospheric pressure (Ustunisik et al. 2011; Tartèse et al. 2013), but alternatively, the Moon may have lost its water earlier during a Moon-forming impact (Shearer et al. 2006; Sharp et al. 2013). Many zircons on the Moon are found in late-forming mesostasis, and zircons can be small or skeletal suggesting rapid crystallization (Meyer et al. 1996; Grange et al. 2009). Conversely, the morphology, large size, and presence in plutonic rocks of other lunar zircons suggest slower growth at depth. It is significant that zircons from lunar plutonic rocks, including four zircons from quartz monzodiorite (15405), are indistinguishable in $\delta^{18}O$ from others on the Moon (Table 1). Taken together, these results are permissive of low or intermediate quantities of water in the lunar magma ocean, but do not support the previous conclusion that mare basalt sources were similar in water content to MORB sources on Earth.

Conclusions

This study shows that zircons are present in the lunar regolith and potentially extend the range of lithologies available for study beyond those in known rocks of the Apollo sample suite. The new high-precision oxygen isotope data show that lunar zircons have a surprisingly narrow range of values that is significantly less fractionated versus mafic whole rocks than analogs in terrestrial ocean crust. The $\delta^{18}O$ and [Ti] data indicate higher temperatures on the Moon for zircon-forming magmas and are consistent with a simple model for lunar zircon formation that includes general equilibration of oxygen isotopes among lunar magmas and late crystallization of zircons in KREEP+Zr-enriched magmas that also concentrated any available water. If additional analyses of lunar zircons from plutonic and volcanic rocks are consistently the same in $\delta^{18}O$, that will strengthen the hypothesis that hydrogen loss pre-dated crystallization of the lunar magma ocean and that the high temperatures of lunar zircons indicate that these magmas were drier than comparable magmas in Earth's mantle.

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